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<p>(21) International Application Number: PCT/GB90/01081 (22) International Filing Date: 13 July 1990 (13.07.90) (30) Priority data: 8916231.7 14 July 1989 (14.07.89) GB (71) Applicant (for all designated States except US): NATIONAL RESEARCH DEVELOPMENT CORPORATION [GB/GB]; 101 Newington Causeway, London SE1 6BU (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : EVANS, Kenneth, Ernest [GB/GB]; 25 Victoria Road, Stockton Heath, Grappenhall, Warrington, Cheshire WA4 2EN (GB). AINSWORTH, Kim, Lesley [GB/GB]; Flat 2, 130 Belmont Road, Liverpool L6 5BJ (GB).</p>		<p>(74) Agent: HAMILTON, Raymond; Patent Department, National Research Development Corporation, 101 Newington Causeway, London SE1 6BU (GB). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.  Published With international search report.</p>
<p>(54) Title: POLYMERIC MATERIALS</p> <div data-bbox="456 1268 1019 1591" data-label="Image"> </div> <p>(57) Abstract</p> <p>Polymers having a microstructure comprising nodes and fibrils may exhibit a negative Poisson ratio. They may be produced by the compaction of a particulate polymer, e.g. UHMW polyethylene and the deformation of the compact by extrusion. The polymers find use in a variety of applications where they are subject to a load.</p>		

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POLYMERIC MATERIALS

This invention relates to novel polymeric materials, to processes for their production and to devices incorporating said materials.

05 All known engineering materials have a positive Poisson ratio, i.e. they contract laterally when stretched and expand laterally when compressed. Materials having a negative Poisson ratio have been postulated as being theoretically possible but only isolated examples have been reported. Recently, in USP 4668557 the preparation of a foamed material having a negative Poisson ratio has been reported. These materials are  
10 produced by compressing conventional open cell foam material under conditions which produce a permanent deformation of the structure of the material.

We have now discovered a further class of materials which exhibit a negative Poisson ratio. This class comprises materials  
15 having a microstructure comprising finite sized particles which are conventionally termed nodes connected by fibrils wherein the microstructure is such that the application of a tension in one direction causes the nodes to be displaced in the transverse direction. This displacement produces the expansion in the  
20 transverse direction which is the characteristic of materials having a negative Poisson ratio. The discovery enables a variety of polymers to be produced in a form which exhibits a negative Poisson ratio and in consequence exhibit a large shear modulus relative to their bulk modulus. Appropriate selection of the  
25 polymer enables materials to be produced which combine this with superior mechanical properties such as the Youngs modulus. This combination of properties can be exploited in a variety of useful devices.

From one aspect our invention provides polymeric materials  
30 having a microstructure comprising nodes interconnected by fibrils which are characterised in that they exhibit a negative Poisson ratio and have a Youngs modulus of at least 0.2 GPa.

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The materials of this invention may be formed from any polymer which is capable of being produced in a form having a microstructure comprising nodes and fibrils. The polymer must be sufficiently ductile to form fibrils when expanded, e.g. by drawing and yet must retain the particulate microstructure which provides the nodes. Not all microstructures comprising nodes and fibrils provide a material having a negative Poisson ratio and the conditions necessary to produce any particular polymer in a form having the desired microstructure may need to be determined by experiment.

We have identified classes of microstructure which are preferably present in the materials of this invention. In a first preferred embodiment the materials comprise a microstructure comprising finite sized particles (nodes) connected by fibrils wherein the length of the fibrils is greater than the shortest distance between the nodes which they connect and wherein the distance between adjacent nodes which are not connected by fibrils is less than maximum distance between fibrils connected to a particular node.

This first type of microstructure is illustrated in Figure 1 which is a cross sectional sketch of such a microstructure. The nodes are represented as cross hatched spheres and the fibrils by the solid lines. Figure 1 illustrates the microstructure prior to the application of a tension in the direction of the x axis.

Figure 2 represents the same cross section after the application of a tension along the x axis (not drawn to scale). The fibrils are now taut and the nodes have been displaced in the direction of the y axis. It is this displacement which gives rise to the negative Poisson ratio.

A second class of microstructure which can give rise to a material having a negative Poisson ratio is one in which the nodes are anisotropic. The useful microstructures are those in which the nodes are aligned in such a way that their longer dimension lies in the direction of the axis of the material and wherein the nodes are connected by fibrils which are longer than the distance between the nodes which they connect.

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Such a microstructure is illustrated in Figure 3 which is a cross-sectional sketch of such a microstructure. The nodes are shown as cross-hatched discoid areas connected by fibrils which are represented by solid lines.

05        Figure 3(a) shows a structure in which the nodes are close together and aligned so that their longest dimension lies along the x axis. Figure 3(b) shows that following the application of a tension along the x axis, the distance between the nodes measured along the x axis has increased. At the same time there  
10        has been some expansion along the y axis by virtue of an interaction between the nodes and fibrils of the type described in relation to Figures 1 and 2. Figure 3(c) shows how the continued application of the tension has caused the nodes to rotate so that their longest dimension is displaced toward the y  
15        axis. This rotation produces the negative Poisson ratio as each "layer" of nodes displaces the adjacent "layer" along the y axis. Figure 3(d) represents the limiting case in which the nodes have rotated so that their longest dimension is now aligned with the y axis.

20        It will be appreciated that sketches 1 to 3 are two dimensional representations which illustrate possible mechanisms whereby the polymers of this invention may exhibit a negative Poisson ratio. In practice the polymers are three dimensional and may well exhibit a microstructure which is not uniform.

25        It is characteristic of the materials of this invention that they exhibit a negative Poisson ratio, i.e. that expansion in the direction of an applied tensile force is accompanied by an expansion in the transverse direction. In this specification all values of Poisson ratio are expressed in terms of the effective  
30        Poisson ratio, i.e. the ratio of the compressive strain measured in the transverse direction to the tensile strain in the direction of the applied tension before that tension is released.

      The materials of this invention may be isotropic or anisotropic. For isotropic materials the minimum Poisson ration  
35        which can be achieved is minus 1. For anisotropic materials the

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minimum Poisson ratio may be much smaller (at least in one direction). The materials may exhibit a ratio which is close to the theoretical limit of minus the square root of the ratio of the maximum Youngs modulus of the material divided by its minimum  
05 Youngs modulus and such materials may be preferred in particular applications. The materials of this invention preferably exhibit a Poisson ratio of less than minus 0.25 and preferably one which is less than minus 0.75 although for the anisotropic materials ratios of as low as minus 10 or minus 12 are attainable and may  
10 be preferred.

The materials of this invention may be formed from any suitable polymer which can be processed to a form having a suitable microstructure. We prefer to utilise a particulate thermoformable polymer as the starting material and to deform a  
15 compacted polymer material under controlled conditions. The polymer should be sufficiently ductile so as to enable it to be deformed under conditions which result in the formation of fibrils and yet retain the particulate microstructure which forms the nodes. Examples of suitable materials include poly-  
20 tetrafluoroethylene and copolymers thereof, polyolefins and copolymers thereof especially polyethylene and copolymers thereof and particularly high molecular weight polyethylene, polypropylene and copolymers thereof, polystyrene and poly(meth)-acrylates.

25 The size of the nodes in the microstructure may vary through a wide range say a maximum dimension of from 0.1  $\mu\text{m}$  to 0.1 mm. The ratio of the fibril length to the length of the maximum dimension of the node should preferably be greater than 1 and more usually will be within the range 1.1:1 to 2.0:1.

30 The polymer from which the materials of this invention are formed will be selected so as to provide the desired properties. Preferably the polymer selected will result in the formation of a material having a Youngs Modulus of at least 1.0 GPa. The materials also preferably have a density of at least  $150\text{Kg}\text{m}^{-3}$  and  
35 more preferably at least  $500\text{Kg}\text{m}^{-3}$ .

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The polymeric materials of this invention may incorporate a filler such as asbestos, carbon black, mica, silica or titanium dioxide. Many examples of compounds used as fillers in polymeric materials are known in the art. Such a filler is preferably  
05 incorporated into the material by mixing with the polymer particles prior to the processing step which is required in order to produce the appropriate microstructure. It is also possible to modify the properties of the polymerised material of the invention by impregnating it with a liquid phase comprising a  
10 monomer or prepolymer for example methyl methacrylate and subsequently polymerising that monomer or prepolymer. This impregnation may be carried out before or after the processing step.

The microstructure of the materials and hence their  
15 properties may also be influenced by the form of the polymer from which they are produced. In particular where the materials are produced from particulate polymer granules the general shape of the particles tends to be retained by the nodes in the microstructure. Thus the use of spherical polymer particles  
20 tends to result in a microstructure having broadly spherical nodes.

The materials may be formed by a process which comprises compacting the polymer particles at elevated temperatures and pressures and deforming the compacted polymer. Thus from a  
25 further aspect this invention provides a process for the production of a polymeric material having a microstructure comprising nodes interconnected by fibrils which exhibits a negative Poisson ration which comprises compacting a particulate polymeric material and deforming the polymer so as to cause it to  
30 expand in at least one direction.

The compaction step preferably comprises heating a mass of polymer particles to a temperature of at least 50°C and more usually at least 90°C. Polymers which have a melting point above these temperatures are preferred for present use. Generally the  
35 temperature should be within 50°C and more preferably within 20°C

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of the melting point of the polymer. The force applied may vary through a wide range, say from 1.0 to 100 MPa. The polymer should preferably be subjected to these conditions for a period which is sufficiently long to allow the entire mass to attain a thermal equilibrium.

Thereafter, the polymers are deformed by expansion in at least one direction until the desired microstructure is obtained. The deformation may be carried out using techniques known in the polymer art such as extrusion drawing or draw assisted extrusion. The deformation is preferably carried out at elevated temperatures say of at least 50°C and more usually of at least 100°C. The polymers may conveniently be produced using conventional polymer extrusion equipment. The polymer powder or granules may be introduced into the barrel of the extruder. They are then conveniently formed into a compacted rod by compression preferably at elevated temperature. Thereafter the polymer may be extruded through a die. The diameter of the die, the temperature at which the polymer is extruded and the speed at which the polymer is extruded may all influence the microstructure of the polymer. The rate of deformation of the polymer should be sufficient to result in the production of the desired microstructure. Too low a rate may not be useful and typically for polyethylene an extrusion rate of greater than 250 or more preferably 500 mm/min may be utilised. The optimum conditions for each polymer may be established by experiment. In general the temperature of the polymer during the extrusion will be at least as high as that used in the compaction step and preferably the temperature may be increased before extrusion commences. Thereafter the extruded material is allowed to cool to ambient temperature. The microstructure of the polymer may be examined using conventional techniques such as scanning electron microscopy. If the polymer does not exhibit the desired microstructure the polymer may be subjected to a further processing step which comprises compressing the polymer in a direction which is perpendicular to the original draw direction.



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Such compression is preferably carried out whilst the drawn polymer is maintained at an elevated temperature generally at least 50°C and preferably at least 90°C. Where particular materials do not exhibit the desired microstructure the parameters of the drawing process may need to be adjusted.

The microstructure of the drawn material may not be uniform. It may comprise regions where the Poisson ratio is higher or even takes a positive value. Nevertheless such materials may be useful on various applications provided that they exhibit a negative Poisson ratio in at least one direction. The materials produced by the process may already be fully drawn out in that direction. Such materials will not exhibit a negative Poisson ratio but may do so following a compression step as described above. Partially drawn materials may also be compressed if desired. The compression may remove all traces of the microstructure from the material but it is characteristic of the materials of this invention that the changes brought about by compression are at least partially reversible and the microstructure may be at least partially restored by extension in the original draw direction.

The materials of this invention find potential use in a variety of applications. They can for example be used to seal a cavity since a plug formed from a material having a negative Poisson ratio will expand laterally when stretched. They also find use in applications wherein compliance of dimension under stress is desirable, e.g. as the interior filler for structural sandwich panels and for shock and vibration absorption. The materials may also find use in a variety of medical applications.

The use of polymeric materials having a negative Poisson ratio in devices in which they are subject to an applied tension compression or shear loading is believed to be novel and constitutes a further aspect of this invention.

The invention is illustrated by the following Example.

Example 1

The barrel of a laboratory manufactured compacted powder

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extruder was filled with an ultra high molecular weight polyethylene powder sold under the Trademark Hostalen GUR 415 by Hoechst (UK) Ltd. of Salisbury Road, Middlesex. The extruder was fitted with a blank die and preheated to a temperature of 110°C.

- 05 The barrel, internal diameter 1 cm and length 8 cm, and contents were allowed to equilibrate for 10 minutes. The plunger was then driven into the barrel by a Schenk mechanical testing machine at a rate of 20 mm/min until a force of 7.31 kN was reached. These conditions were maintained for 20 minutes. The  
10 result was a compacted polyethylene rod.

- The extruder was then fitted with a die having a diameter of 5 mm and an entry angle of 45°. The temperature was maintained at 160°C for a further 20 minutes. The plunger was then driven into the barrel at a rate of 500 mm/min. The  
15 extrudate comprised a rod having the appearance shown in Figure 4.

- The Poisson ratio of the extrudate was determined by applying compressive strains in the directions indicated in Figure 4. Photographs were taken of the specimen before and after compression was applied. From the change in dimensions measured  
20 from the photographs the Poisson ratio was calculated as the ratio of compressive strain transverse to loading direction to tensile strain along loading direction. The load was released and the compression repeated up to six times. The results for eight specimens each prepared by the above experimental procedure  
25 were as follows:

A. Compression in direction 1

Specimen No. 1

Section No.		Poisson's ratio for	
		1st compression	2nd compression
30	1	-1.00	-0.71
	2	0.00	0.00
	3	-0.50	-2.07
	4	-0.69	-1.37
	5	-2.47	-4.35

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Specimen No. 2

Section No.		Poisson's ratio for 1st compression
05	1	-1.21
	2	0.00
	3	-1.11
	4	0.00
	5	0.00
	6	-1.00

10 Specimen No. 3

Section No.		Poisson's ratio for	
		1st compression	2nd compression
15	1	0.00	0.00
	2	-0.48	-0.21
	3	0.00	0.23
	4	0.00	-0.29
	5	-0.73	0.00

Specimen No. 4 - a) left hand end

Section No.		Poisson's ratio for 1st compression
20	1	-2.22
	2	-0.58
	3	0.00
	4	-1.50
25	5	-0.62

b) middle section

Section No.		Poisson's ratio for	
		1st compression	2nd compression
30	1	-0.96	0.00
	2	0.00	-1.13
	3	0.00	-0.32
	4	-0.46	-1.00
	5	-0.74	-0.43
	6	-0.34	-0.47
35	7	0.00	-0.52

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c) right hand end

Section No.	Poisson's ratio for 1st compression
1	0.00
05 2	-0.81
3	-0.49

N.B. This specimen was split into three parts as it was too long to be tested in one piece.

Specimen No. 5

Section No.	Poisson's ratio for compression No.				
	1	2	3	4	5
1	-0.31	-0.18	-0.27	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00
3	-0.41	0.00	0.00	-0.18	-0.19
15 4	-0.23	-0.20	-0.32	-0.35	-0.25
5	-0.45	-0.39	-0.64	-0.53	-0.47
6	-0.43	-0.45	-0.57	-0.18	-0.52

Specimen No. 6

Section No.	Poisson's ratio for compression No.					
	1	2	3	4	5	6
20 1	-0.13	-0.26	-0.49	-0.24	-0.61	-0.26
2	0.00	0.00	0.00	0.00	-0.64	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00
4	-0.20	-0.28	-0.34	-0.28	-0.25	-0.19
25 5	-0.16	-0.31	-0.26	-0.66	-0.31	-0.30
6	-0.20	-0.27	-0.34	-0.29	-0.36	-0.25

B. Compression in direction 2Specimen No. 7

Section No.	Poisson's ratio for	
	1st compression	2nd compression
30 1	-0.05	-0.06

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Specimen No. 8

Section No.

Poisson's ratio for

1st compression

2nd compression

	1	0.00	-0.04
05	2	+0.19	+0.22
	3	+0.03	+0.05

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CLAIMS

1. A polymeric material having a microstructure comprising nodes interconnected by fibrils which is characterised in that it has a negative Poisson ratio and a Young's modulus of at least 0.2 GPa.
2. A material according to Claim 1 characterised in that the  
05 polymer is selected from the group comprising homo or co-polymers of poly tetrafluoroethylene, homo and copolymers of polyolefins polystyrene and poly(meth)acrylate.
3. A material according to Claim 2 characterised in that the polymeric material is a homo or copolymer of polyethylene.
- 10 4. A material according to Claim 3 characterised in that the polymeric material is a ultra-high molecular weight polyethylene.
5. A material according to any of Claims 1 to 4 characterised in that it comprises a filler.
6. A material according to any of Claims 1 to 5 characterised in  
15 that it has a Young's modulus of at least 1.0 GPa.
7. A material according to any of the preceding claim characterised in that it has a density of at least  $150 \text{ kg m}^{-3}$ .
8. A process for the production of a material according to any of Claims 1 to 7 wherein a polymer mass is deformed at elevated  
20 temperature and the desired microstructure is produced.
9. A process according to Claim 8 characterised in that the deformation is carried out by extrusion drawing or draw assisted extrusion.
10. A process according to either of Claims 8 or 9 characterised  
25 in that the polymer mass is drawn at an elevated temperature.
11. A process according to Claim 10 characterised in that the temperature is at least  $100^\circ\text{C}$ .
12. A process according to any of Claims 8 to 11 characterised in that the drawing is effected by the extrusion of the polymer  
30 through a die.
13. A process according to any of Claims 8 to 12 characterised in that the polymer mass to be deformed is formed by a process of compacting polymer particles and maintaining the compacted mass at an elevated temperature.

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14. A process according to Claim 13 characterised in that the compacted mass is maintained at a temperature of at least 90°C.
15. A process according to either of Claims 13 or 14 characterised in that the mass is maintained at a temperature
- 05 which is within 50°C of the melting point of the polymer.
16. A process according to any of Claims 13 to 15 characterised in that the polymer mass is formed by compaction at a pressure of from 1.0 to 100 MPa.
17. A process according to any of Claims 13 to 16 characterised
- 10 in that the pressure is maintained throughout the period in which the mass is maintained at an elevated temperature.
18. A process according to any of Claims 8 to 17 characterised in that the deformed polymer is subsequently subject to a compression in a direction which is perpendicular to the draw
- 15 direction.
19. The use of a polymeric material having a microstructure which comprises nodes interconnected by fibrils and a negative Poisson ratio in devices in which the polymer is subjected to an applied tension compression or shear loading.

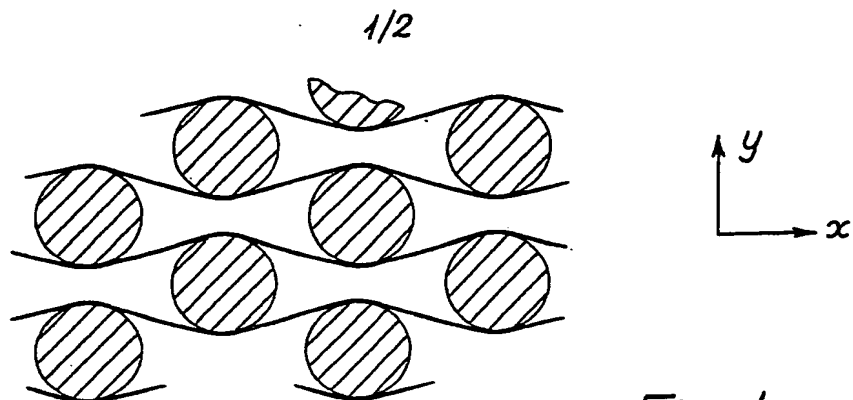


Fig. 1

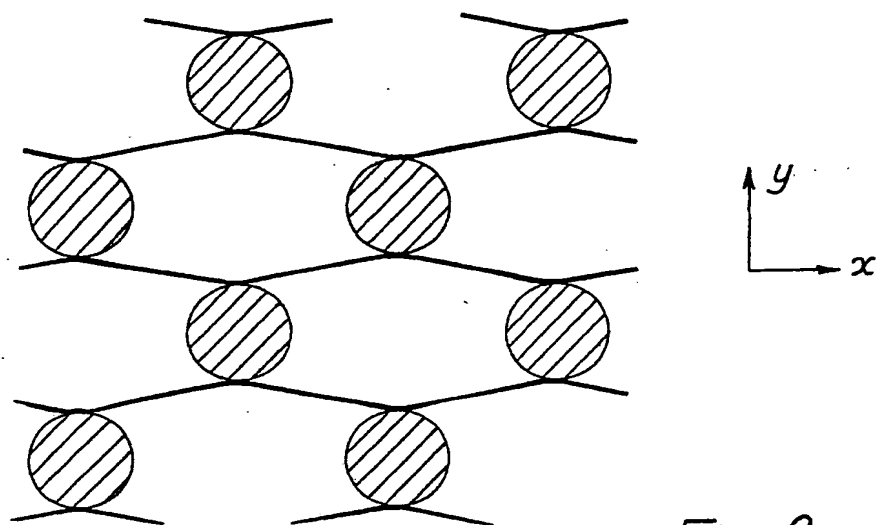


Fig. 2

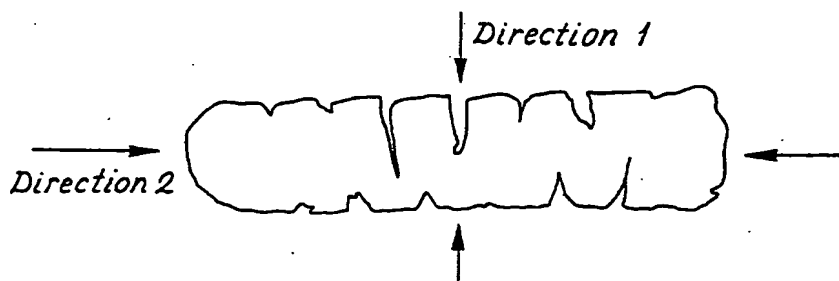
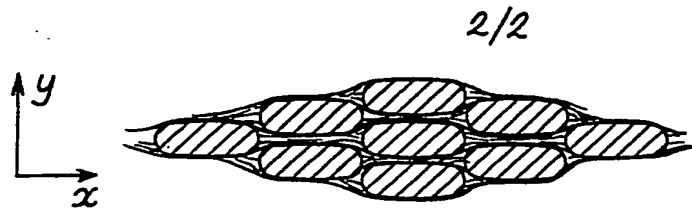
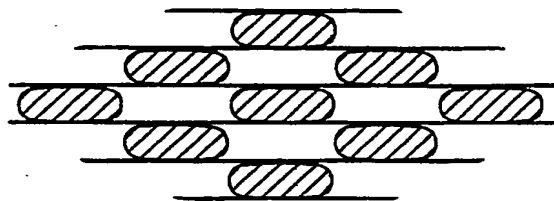


Fig. 4

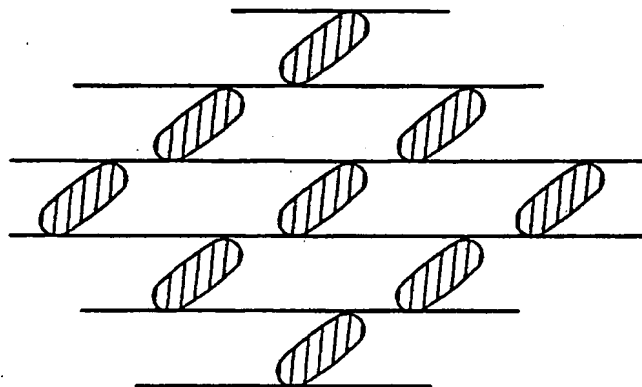




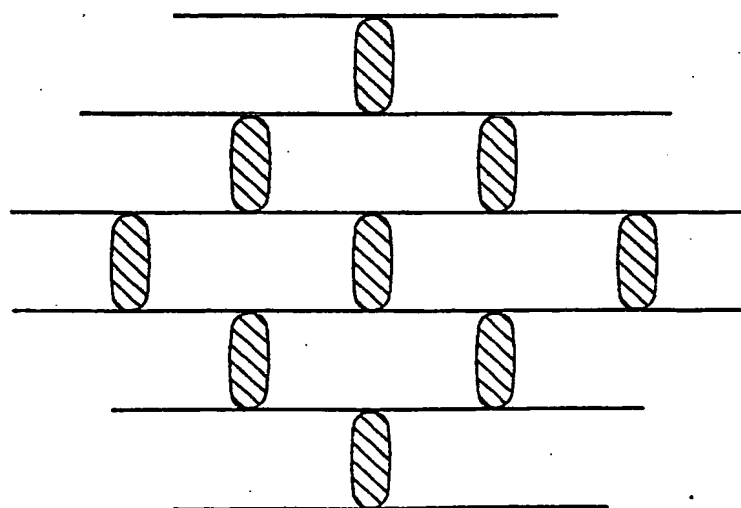
*Fig. 3a*



*Fig. 3b*



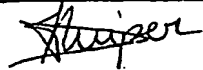
*Fig. 3c*



*Fig. 3d*

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01081

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>5</sup> : B 29 C 55/00, B 29 C 55/30, // B 29 K 27:18, 23:00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System <sup>1</sup>	Classification Symbols	
IPC <sup>5</sup>	B 29 C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP, A, 0267719 (W.L. GORE & ASSOCIATES) 18 May 1988 see column 3, line 58 - column 4, line 47; column 6, lines 36-47; figure 6 --	1-19
X	EP, A, 0313263 (W.L. GORE & ASSOCIATES) 26 April 1989 see claim 12; figure 2 --	1-19
X	EP, A, 0253513 (NIPPON OIL) 20 January 1988 see page 5, lines 26-55 --	1-19
X	US, A, 4279245 (TAKAGI ET AL.) 21 July 1981 see column 2, lines 56-66; column 3, line 51; figure 3 --	1-19
./.		
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15th October 1990	06. 11. 90	
International Searching Authority	Signature of Authorized Officer:	
EUROPEAN PATENT OFFICE	Mme N. KUIPER 	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	US, A, 4482516 (BOWMAN et al.) 13 November 1984 see example 3 --	1-19
P,X	Journal of Physics D: Applied Physics, volume 22, no. 12, November 1989, IOP Publishing Ltd, (GB), B.D. Caddock et al.: "Microporous materials with negative poisson's ratios: I. microstructure and mechanical properties", pages 1877-1882 see paragraphs 2.1, 2.2, 2.3 --	1-19
A	US, A, 4668557 (LAKES) 26 May 1987 see column 4, line 47 - column 6, line 2 (cited in the application) -----	1-19

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9001081

SA 38599

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 29/10/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0267719	18-05-88	US-A- 4743480	10-05-88
		AU-A- 5682990	27-09-90
		AU-B- 600730	23-08-90
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		GB-A- 2197870	02-06-88
		JP-A- 63139926	11-06-88
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